

F-8766

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Seiko HIRAYAMA, et al.
Serial No. : 10/549,585
Filed : December 1, 2005
For : PHOSPHOR AND METHOD FOR
PRODUCING SAME
Group Art Unit : 1621

Examiner : Kevin M. Johnson

Assistant Commissioner for Patents
Washington, D.C. 20231

VERIFICATION OF TRANSLATION

Sir: Fumio Akiyama, residing at MT-2 BLDG., 5-36, Miyahara 3-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0003 JAPAN, declares that he is fluent in Japanese and English and that the herewith submitted English translations of the certified copies of the priority documents in the above identified application, which were originally written in Japanese, are a true and accurate literal translations.

He further declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Name: Fumio Akiyama

Signature: 

Date: December 11, 2008

Submission Date: July 30th, Heisei-15 (2003)
Number=SA61 JP Patent Application No.2003-282828

[Document Name] Patent Application
[Filing Number] SA61
[To] Commissioner, Patent Office
[IPC] C09K 11/08
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] HIRAYAMA Seiko
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] KOBAYASHI Keita
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] ISHII Junya
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] WADA Mizuho
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] NAKAHARA Shinji
[Applicant]
[Identification Number] 000174541
[Name] Sakai Chemical Industry Co., Ltd.
[Agent]
[Identification Number] 100086586
[Patent Attorney]
[Name] YASUTOMI Yasuo
[Appointed Agent]
[Identification Number] 1000120019
[Patent Attorney]
[Name] YAGI Toshiyasu

Submission Date: July 30th, Heisei-15 (2003)
Number=SA61 JP Patent Application No.2003-282828

[Indication of Fee]

[Number of Deposit Ledger] 033891

[Amount of Payment] 21,000 yen

[List of Attached Documents]

[Document Name] Claims 1

[Document Name] Description 1

[Document Name] Abstract 1

[The Number of General Power of Attorney] 0004000

[Document Name] Claims

[Claim 1]

An alkaline earth metal aluminate phosphor containing bivalent europium as an activator,

5 which is obtained by a process comprising;

a step (1) of mixing a fired product (A) with a compound (B),

said fired product (A) comprising barium and/or strontium(a), magnesium(b), aluminum(c) and europium(d),

10 said compound (B) being at least one compound selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and

15 a step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the step (1) or a fired product of the mixture obtained in the step (1),

said step (2) being preceded, at least once, by firing in a reducing atmosphere.

20

[Claim 2]

The alkaline earth metal aluminate phosphor according to Claim 1,

25 wherein said fired product (A) contains at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead.

[Claim 3]

30 The alkaline earth metal aluminate phosphor according to Claim 1 or 2,

wherein said firing in a reducing atmosphere is applied to the mixture obtained in the step (1).

35 [Claim 4]

The alkaline earth metal aluminate phosphor according to Claim 1, 2 or 3,

wherein said firing in a reducing atmosphere is carried out on the occasion of firing for producing the fired product
5 (A) comprising barium and/or strontium(a), magnesium(b), aluminum(c) and europium(d).

[Claim 5]

The alkaline earth metal aluminate phosphor according to
10 any one of Claims 1 to 4,

which has a powder whiteness of not lower than 85 as expressed in terms of W value.

[Claim 6]

15 The alkaline earth metal aluminate phosphor according to any one of Claims 1 to 5,

wherein the content of at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead is within the range of
20 0.0001 to 0.01 mole per mole of the aluminum element.

[Claim 7]

The alkaline earth metal aluminate phosphor according to any one of Claims 1 to 6,

25 wherein the alkaline earth metal aluminate phosphor containing bivalent europium as an activator is represented by the following general formula (1):



in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and
30 Y satisfies the relationship of $0 < Y \leq 0.2$.

[Claim 8]

A method of producing alkaline earth metal aluminate phosphor containing bivalent europium as an activator,
35 wherein the method comprises;

a step (1) of mixing a fired product (A) with a compound (B),

said fired product (A) comprising barium and/or strontium(a), magnesium(b), aluminum(c) and europium(d),

5 said compound (B) being at least one compound selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and

10 a step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the step (1) or a fired product of the mixture obtained in the step (1),

said step (2) being preceded, at least once, by firing in a reducing atmosphere.

15

[Claim 9]

The method of producing alkaline earth metal aluminate phosphors according to Claim 8,

20 wherein said fired product (A) contains at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead.

[Document Name] DESCRIPTION

[Title of the Invention] PHOSPHOR AND METHOD OF PRODUCING SAME

[Technical Field of the Invention]

[0001]

5 The present invention relates to an alkaline earth metal aluminate phosphor and a method of producing the same.

[Background Art]

[0002]

10 In recent years, various phosphors have been used in plasma display panels (hereinafter referred to as PDPs). Among such phosphors, alkaline earth metal aluminate phosphors containing bivalent europium as an activator, for example (Ba,Sr)MgAl₁₀O₁₇:Eu²⁺, are used as blue phosphors.

[0003]

15 When exposed to elevated temperatures or to vacuum ultraviolet rays, ultraviolet rays or the like for phosphor excitation, such alkaline earth metal aluminate phosphors containing bivalent europium as an activator deteriorate and decrease in luminance. The mechanism so far proposed as the
20 cause therefor consists in the oxidation of bivalent Eu, which forms luminescence centers in the blue phosphors, in particular, to the trivalent form due to the oxidative effect of heating on the phosphor surface, resulting in the loss of bivalent blue luminescence centers and the decrease in luminance.

25 [0004]

 In particular, the phosphors may be subjected to heating at elevated temperatures in the step of molding for use in certain fields of application, and therefore, it would be problematic. In the process of manufacturing PDPs, for
30 instance, partitions called ribs are formed on the back face glass sheet, and the respective fluorescence substances each in the form of a paste prepared by using a binder and a solvent are applied to respective partition-surrounded areas without color mixing. The glass sheet is then heated at 400 to 500°C
35 for binder elimination in the manner of firing and for fusion

bonding to a front face glass sheet. It is suggested that, in such a firing step, the firing is carried out in a high humidity environment as a result of not only the oxidative action but also the evaporation of the moisture originally contained in dielectrics, electrodes and other materials than the phosphors, possibly affecting the fluorescent materials. Therefore, as far as blue phosphors are concerned, it is a great subject to inhibit luminance decreases as well as emission shifting in the heating/firing step.

10 [0005]

Some attempts have already been made to prevent the deterioration by chemical treatment of the phosphor surface (e.g. Patent document 1, Patent document 2, and Patent document 3). However, these methods consist in coating the surface with boric acid or a compound of such an element as antimony or silica and thereby preventing luminance decreases. Therefore, it is difficult to entirely prevent the oxidative deterioration.

[0006]

Another problem is that a phosphor, once colored and reduced in powder whiteness, absorbs the fluorescence emitted, resulting in reduced function. Therefore, it is desirable that the phosphor has high powder whiteness. As means for preventing the luminance of a phosphor from decreasing, there has been disclosed a method of producing phosphors which comprises firing in a reducing atmosphere, followed by firing in an oxidizing atmosphere (e.g. Patent document 4). Such method, however, is a method of producing alkaline earth metal silicoaluminate phosphors but is not intended for producing alkaline earth metal aluminate phosphor.

30 [0007]

[Patent Document 1] JP-10-195428 A

[Patent Document 2] JP-10-298548 A

[Patent Document 3] JP-10-204429 A

[Patent Document 4] JP-2002-348570 A

35 [Problem to be solved by the invention]

[0008]

In view of the foregoing, it is an object of the present invention to provide an alkaline earth metal aluminate phosphor that does not cause luminance decreases and emission shifting but have good heat resistance durability against vacuum ultraviolet rays and ultraviolet rays, and high powder whiteness. It is another object of the present invention to provide a method of producing the same.

[Means for solving the Problem]

10 [0009]

The present invention relates to an alkaline earth metal aluminate phosphor containing bivalent europium as an activator, which is obtained by a process comprising:

15 a step (1) of mixing a fired product (A) with a compound (B),

the fired product (A) comprising barium and/or strontium(a), magnesium(b), aluminum(c) and europium(d),

20 the compound (B) being at least one compound selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and

a step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the step (1) or a fired product of the mixture obtained in the step (1),

25 the step (2) being preceded, at least once, by firing in a reducing atmosphere.

30 The fired product (A) may further contain at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead.

The above-mentioned firing in a reducing atmosphere may be applied to the mixture obtained in the step (1).

35 Preferably, the above-mentioned firing in a reducing atmosphere may be carried out on the occasion of firing for producing the fired product (A) comprising barium and/or

strontium(a), magnesium (b), aluminum(c) and europium(d).

[0010]

Preferably, the above-mentioned alkaline earth metal aluminate phosphor has a powder whiteness of not lower than 85
5 as expressed in terms of W value.

In the above-mentioned alkaline earth metal aluminate phosphor, the content of at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead is preferably within
10 the range of 0.0001 to 0.01 mole per mole of the aluminum element.

The above-mentioned alkaline earth metal aluminate phosphor containing bivalent europium as an activator is preferably represented by the following general formula (1):



15 in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and Y satisfies the relationship of $0 < Y \leq 0.2$.

[0011]

The present invention also relates to a method of producing alkaline earth metal aluminate phosphors containing
20 bivalent europium as an activator,

which comprises;

a step (1) of mixing a fired product (A) with a compound (B),

the fired product (A) comprising barium and/or
25 strontium(a), magnesium(b), aluminum(c) and europium(d),

the compound (B) being at least one compound selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and

30 a step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the step (1) or a fired product of the mixture obtained in the step (1),

the step (2) being preceded, at least once, by firing in a reducing atmosphere.

35 The fired product (A) may further contain at least one

element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead.

In the following, the present invention is described in detail..

[0012]

The phosphor of the invention is an alkaline earth metal aluminate phosphor containing bivalent europium as an activator. Usable as the base phosphor are generally known ones, and there may be mentioned, for example, alkaline earth metal aluminate phosphors comprising barium and/or strontium, europium, magnesium, aluminum and oxygen. Preferred as such alkaline earth metal aluminate phosphors are those represented by the following general formula (1):



in the formula, X satisfies the relationship of $0 \leq X \leq 0.3$ and Y satisfies the relationship of $0 < Y \leq 0.2$.

[0013]

The alkaline earth metal aluminate phosphor of the invention is an alkaline earth metal aluminate phosphor containing bivalent europium as an activator and contains at least one element selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead. The above element may occur either within the alkaline earth metal aluminate phosphor or on the surface in a localized manner, such as resulting from surface treatment with a compound of that element. Preferably, however, it occurs within the alkaline earth metal aluminate phosphor. The phosphor may contain two or more above element species simultaneously or contain only one above element species. Among the elements enumerated above, tungsten, niobium and bismuth are preferred, since they give phosphors having good heat resistance and durability against vacuum ultraviolet rays and ultraviolet rays, among others; and tungsten is most preferred.

[0014]

The content of the at least one above element selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead in the alkaline earth metal aluminate phosphor of the invention is preferably within
5 the range of 0.0001 to 0.01 mole per mole of the aluminum element. At levels lower than 0.0001 mole, the effects of the addition will be little and, at levels exceeding 0.01 mole, the luminance will unfavorably become excessively low. The content level range differs depending on the element species employed. In
10 the case of tungsten and/or niobium, for instance, a preferred lower limit to the above range is 0.0003 mole, and a preferred upper range is 0.007 mole. Further, a most preferred lower limit to the above range is 0.0005 mole, and a most preferred upper limit is 0.003 mole. The content of the above element
15 can be adjusted to a level within a specific range by adjusting the mixing ratio between the precursor compound of aluminum and the precursor compound of the above-mentioned element in the mixture of the precursor compounds used as the starting materials.

20 [0015]

The alkaline earth metal aluminate phosphor of the invention may further contain one or more elements other than the above element at levels at which they will never adversely affect the physical properties of the phosphor. Since, however,
25 the presence of an impurity may influence the luminance, heat resistance, durability against vacuum ultraviolet ray and so forth, the content of elements other than the essential components should preferably be lower than 1%.

[0016]

30 The alkaline earth metal aluminate phosphor of the invention is obtainable by a process comprising; the step (1) of mixing a fired product (A) with a compound (B), wherein the fired product (A) comprises barium and/or strontium(a), magnesium (b), aluminum (c) and europium(d), and the compound
35 (B) is at least one compound selected from the group consisting

of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and the step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the
5 above step (1) or a fired product of the mixture obtained in the above step (1), wherein the step (2) is preceded, at least once, by further firing in a reducing atmosphere.

[0017]

The process comprises adding is at least one compound (B)
10 selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds, then firing in a reducing atmosphere at least once, and, after the step of firing under a reducing
15 atmosphere, firing in an oxidizing atmosphere. This specific firing process provides sufficient whiteness to an alkaline earth metal aluminate phosphor, and prevents the phosphor from luminescence decrease and emission shifting.

[0018]

The fired product (A) is a fired product comprising barium
20 and/or strontium (a), magnesium (b), aluminum (c) and europium (d) and can be prepared, for example, by firing a mixture of precursor compounds of barium and/or strontium (a), magnesium (b), aluminum (c) and europium (d), respectively. The
25 above-mentioned precursor compounds each is not particularly restricted but may be any oxides or any other compounds capable of being converted to an oxide upon firing.

[0019]

The precursor compound of barium is not particularly
30 restricted but includes, for example, barium oxide, barium carbonate, barium nitrate, barium sulfate, barium sulfide, barium chloride and barium hydroxide. The precursor compound of strontium is not particularly restricted but includes, for example, strontium oxide, strontium carbonate, strontium
35 nitrate, strontium sulfate, strontium sulfide, strontium

chloride and strontium hydroxide. The precursor compound of magnesium is not particularly restricted but includes, for example, magnesium oxide, basic magnesium carbonate and magnesium hydroxide. The precursor compound of aluminum is not particularly restricted but includes, for example, aluminum oxide, aluminum nitrate, aluminum sulfate and aluminum chloride. The precursor compound of europium is not particularly restricted but includes, for example, europium oxide, europium carbonate, europium chloride and europium acetate. The oxidation number of the metal element is not particularly restricted, either.

[0020]

The fired product (A) may further contain at least one element (e) selected from the group consisting of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead. Namely, the above steps (1) and (2) may be carried out using fired product (A) that contains the above element.

[0021]

The fired product (A) which contains the element (e) can be prepared by adding a desired amount of a precursor compound of at least one element (e) selected from the group consisting of tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead to a mixture of precursor compounds of (a) to (d), respectively. The precursor compound of the element (e) is not particularly restricted but an oxide or any other compound capable of being converted to an oxide upon firing can be used. Examples of the precursor compound of the element (e) include compounds to be used as the compound (B), which will be mentioned below.

[0022]

The compounds to be used as the precursor compounds each preferably has a purity as high as possible and, in particular, is preferably free of any impurity other than the volatile constituents or contains only a slight amount of such an impurity. If such an impurity is present in a starting material,

the physical properties of the product alkaline earth metal aluminate phosphor may unfavorably be modified. It is preferable that each starting material have a purity of 99% or higher. The above-mentioned respective precursor compounds
5 are blended together, to give a mixture, in such proportions that they give the proportions of the respective elements in the alkaline earth metal aluminate phosphor to be produced.

[0023]

In producing the fired product (A), a flux may further
10 be used. The flux is not particularly restricted but is preferably one capable of functioning as a growth promoter of the fired product and volatilizing without influencing the composition of the phosphor, for example magnesium fluoride or aluminum fluoride.

15 [0024]

The mixture of the precursor compounds, if necessary further containing the flux, can be prepared mixing together the respective components mentioned above by any of the conventional methods.

20 The method of mixing is not particularly restricted but may be any of those capable of causing homogeneous mixing without allowing aggregation of each individual component. More specifically, there may be mentioned, for example, the dry mixing method using a ball mill or blender, for instance; the
25 method comprising wet mixing in the presence of a solvent using a homogenizer or a like agitator, a ball mill, a bead mill or a like media grinder, followed by drying; the method comprising preparing an aqueous solution of precursor compounds each in a water-soluble salt form, precipitating the precursor each in
30 an insoluble salt form by pH adjustment with a pH adjusting agent so as to give a predetermined composition, washing the precipitate and drying the same; and the method comprising preparing an aqueous solution of precursor compounds each in a water-soluble salt form, then preparing a W/O type emulsion
35 using the solution and an oil, together with a dispersant,

heating and dehydrating the emulsion and recovering the resulting oleaginous dispersion of the precursor mixture.

[0025]

5 The fired product (A) can be obtained, for example, by carrying out an arbitrary number of repetitions of the step of firing in an oxidizing atmosphere, such as the ambient atmosphere or a nitrogen-oxygen mixed gas atmosphere. The firing is preferably carried out at a temperature within the range of 1000 to 1700°C. The reaction time in the firing in
10 a reducing atmosphere varies depending on the reaction temperature and, for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the desired alkaline earth metal aluminate phosphor can be obtained with great efficiency.

15 [0026]

Alternatively, the fired product (A) can be obtained by firing the above mixture in a reducing atmosphere. The firing is preferably carried out at a temperature within the range of 1000 to 1700°C. When the firing temperature is lower than
20 1000°C, the fluorescence center europium is not sufficiently reduced, and the luminance of resultant phosphor becomes poor. Temperatures higher than 1700°C may give excessively large particles and cause marked deteriorations in performance characteristics, unfavorably making particle dispersion
25 difficult due to strong intercrystalline fusion bonding and thus markedly inhibiting uniform fluorescent film formation. The above-mentioned firing is required to be carried out in a reducing atmosphere so that the fluorescence center europium may be reduced. Thus, the firing is carried out in a reducing
30 atmosphere.

[0027]

The reducing atmosphere conditions are not particularly restricted but the firing is carried out, for example, in a nitrogen-hydrogen mixed gas atmosphere. In the firing in a
35 nitrogen-hydrogen mixed gas atmosphere, the mixing ratio of

nitrogen to hydrogen is preferably 99.9/0.1 to 80/20 (by volume).

[0028]

5 The reaction time in the firing in a reducing atmosphere varies depending on the reaction temperature and, for the reaction to proceed satisfactorily, a reaction time of 0.5 to 10 hours, for instance, is employed, whereupon the desired alkaline earth metal aluminate phosphor can be obtained with great efficiency.

10 [0029]

The fired product (A) may also be one obtained by the above-mentioned optional firing in an oxidizing atmosphere and the subsequent firing in a reducing atmosphere. It may also be one obtained by a plurality of repetitions of the
15 above-mentioned firing in an oxidizing atmosphere and the firing in an oxidizing atmosphere.

[0030]

The step (1) in the present invention is the step of mixing up the fired product (A) obtained in the above manner with at
20 least one compound (B) selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compounds, thallium compounds and lead compounds.

[0031]

25 The compound (B) is not particularly restricted but, like in the case of the precursor compounds mentioned above, an oxide or any other compound capable of being converted to an oxide upon firing can be used.

The precursor compound of indium is not particularly
30 restricted but includes, for example, indium oxide, indium trichloride, indium nitrate, indium hydroxide and indium sulfate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of tungsten is not particularly restricted but includes, for
35 example, tungsten oxide, ammonium tungstate and tungsten

hexachloride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of niobium is not particularly restricted but includes, for example, niobium oxide and niobium pentoxide. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of bismuth is not particularly restricted but includes, for example, bismuth oxide and bismuth nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of molybdenum is not particularly restricted but includes, for example, molybdenum oxide, ammonium molybdate and molybdenum chloride. The oxidation number of the metal element is not particularly restricted, either.

[0032]

The precursor compound of tantalum is not particularly restricted but includes, for example, tantalum oxide, tantalum chloride and tantalum fluoride. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of thallium is not particularly restricted but includes, for example, thallium oxide, thallium carbonate and thallium nitrate. The oxidation number of the metal element is not particularly restricted, either. The precursor compound of lead is not particularly restricted but includes, for example, lead oxide, lead carbonate and lead nitrate. The oxidation number of the metal element is not particularly restricted, either.

[0033]

The compound (B) each preferably has a purity as high as possible and, in particular, is preferably free of any impurity other than the volatile constituents or contains only a slight amount of such an impurity, just as precursor compounds to be used as starting materials for the fired product (A). If such an impurity is present in a starting material, the physical properties of the product alkaline earth metal aluminate phosphor may unfavorably be modified. It is preferable that

each starting material have a purity of 99% or higher.

[0034]

The method of mixing up the fired product (A) with the compound (B) in the step (1) is not particularly restricted but
5 mention may be made, for example, of the dry mixing method using a ball mill or a blender, and the method comprising wet mixing in the presence of a solvent using an agitator such as a homogenizer or a media grinder such as a ball mill or a bead mill, followed by drying. The step (1) is preferably carried
10 out using such a method, whereupon the fired product (A) can be ground and at the same time mixed with the compound (B).

[0035]

The mixture obtained in the step (1) may be further fired and then submitted to the step (2) mentioned above. The firing
15 following the step (1) may be carried out either in an oxidizing atmosphere or in a reducing condition. Conditions for firing in an oxidizing atmosphere and firing in a reducing atmosphere may be carried out in the same manner as firing in a process for producing the fired product (A).

20 [0036]

In producing the phosphor of the invention, the firing in a reducing atmosphere is carried out at least once prior to the above-mentioned step (2). When the firing in a reducing atmosphere is carried out at least once, europium is reduced
25 and a phosphor with a sufficient level of luminance can be obtained. Preferably, the firing in a reducing atmosphere is applied to the mixture obtained in the above-mentioned step (1), or it is carried out in the step of firing for obtaining the fired product (A). When the firing in a reducing atmosphere
30 is carried out in the step of firing for obtaining the fired product (A), the firing in the reducing atmosphere is preferably carried out after firing in an oxidizing atmosphere.

[0037]

The above-mentioned step (2) is the step of firing, in
35 an oxidizing atmosphere, the mixture obtained in the

above-mentioned step (1). The firing in an oxidizing atmosphere makes it possible to attain such objects as the prevention of decreases in luminance and of luminous color shifting while retaining the powder whiteness of the phosphor.

5 [0038]

The firing in an oxidizing atmosphere in the step (2) is not particularly restricted, but mention may be made of the firing in the ambient atmosphere or in a nitrogen-oxygen mixed gas atmosphere, for instance. The firing in a nitrogen-oxygen
10 mixed gas atmosphere is preferred among others since the oxidation of europium functioning as an activator can then be prevented as far as possible. The mixing ratio between nitrogen and oxygen in the above-mentioned mixed gas is not particularly restricted but the nitrogen/oxygen ratio is preferably 99.9/0.1
15 to 95/5 (by volume) so that the oxidation of europium may be inhibited.

[0039]

The nitrogen-oxygen mixed gas may retain the same mixing ratio from the initial stage to the end point of the firing.
20 Alternatively, oxygen may be injected into the atmosphere in the course of firing. On that occasion, the temperature, duration and time for or of oxygen injection are not particularly restricted but can be selected arbitrarily. The firing in an oxidizing atmosphere is preferably carried out in
25 temperature range from the lower limit of 500°C to the upper limit of 1000°C so that the oxidation of europium may be inhibited as far as possible. The maximum temperature, after arrival thereof, is preferably maintained for 0 to 20 hours.

[0040]

30 The alkaline earth metal aluminate phosphor fired in an oxidizing atmosphere is preferably ground to adjust the particle diameter. Usable as the grinder to be used in the above-mentioned grinding are dry grinders such as hammer mills, fluid energy mills and mixing mullers, and wet grinders such
35 as ball mills and bead mills. In the above-mentioned grinding,

excessively intense grinding may result in marked deteriorations in phosphor characteristics and, therefore, it is necessary to select an adequate grinder or mill and employ best working conditions. The classification procedure using
5 a liquid cyclone or the like may also be properly utilized. Such a method of producing alkaline earth metal aluminate phosphors as mentioned above also constitutes an aspect of the present invention.

[0041]

10 The alkaline earth metal aluminate phosphor of the invention has high powder whiteness owing to the above process. The powder whiteness of the alkaline earth metal aluminate phosphor is preferably not lower than 85 as expressed in terms of W value. The W value is calculated from the values of L
15 (brightness), a (chroma) and b (hue) according to Hunter's color model, by using the following formula (2):

$$W = 100 - \{(100 - L)^2 + (a^2 + b^2)\}^{1/2} \quad (2)$$

When the W value is smaller than 85, high levels of absorption of the fluorescence emitted will result and,
20 possibly, no good phosphor performance characteristics may be acquired. More preferably, the W value is 90 or higher.

[0042]

The alkaline earth metal aluminate phosphor with a powder whiteness of not lower than 85 as expressed in terms of W value
25 is preferred since it will not absorb the fluorescence emitted but can send out fluorescence efficiently. Powder whiteness varies depends on various factors, such as a type or amount of the compound (B), firing conditions or firing time in production process. Thus, selection of these ingredients or control of
30 production conditions enables to provide a phosphor with a powder whiteness of not lower than 85.

[0043]

The alkaline earth metal aluminate phosphor of the invention is excellent in quality also from the viewpoint that
35 the luminous color shifting is inhibited. The luminous color

shifting so referred to herein is the change in chromaticity of the light emitted by the alkaline earth metal aluminate phosphor, and a smaller change in chromaticity of the light emitted indicates a smaller change in luminous color, hence a higher degree of inhibition of luminous color shifting. The change in chromaticity of the light emitted can be calculated using the chromaticity (y) of the light emitted by the phosphor as measured by using a luminance meter (e.g. Otsuka Electronics model MCPD-3000) according to the following formula (3):

10 $\Delta y = \text{chromaticity (y2) of the light emitted after firing, ultraviolet irradiation, etc.} - \text{chromaticity (y1) of the light emitted by the phosphor in powder form}$ (3)

[0044]

For example, a phosphor for which the change in chromaticity (Δy) of the light emitted between the measurement immediately after preparation and the measurement after the heating step comprising heating in the air at a rate of 150°C per hour, maintaining the temperature of 500°C for 1 hour and then cooling at a rate of 150°C per hour is smaller than 0.01 can be regarded as being inhibited from luminous color shifting. When the change exceeds 0.01, the change in luminous color is great and the luminous color shifting inhibiting performance is unsatisfactory. More preferably, the above-mentioned change in chromaticity is not greater than 0.007.

25 [Effect of the Invention]

[0045]

The alkaline earth metal aluminate phosphor of the invention is excellent in heat resistance and in durability against vacuum ultraviolet rays or ultraviolet rays, and shows no luminance reduction or luminous color shifting, hence can be properly used in PDPs and in like applications. Furthermore, the above alkaline earth metal aluminate phosphor shows a high powder whiteness and therefore is excellent in fluorescence-emitting capacity.

35 [Examples]

[0046]

The following examples further illustrate the present invention. They are, however, by no means limitative of the scope of the invention.

5

(Example 1)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33
10 g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium(III) oxide (purity on analysis: 99.6% by weight) and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an
15 automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours,
20 followed by temperature lowering at a rate of 200°C per hour. Indium oxide (special reagent grade), 0.198 g was weighed using an electronic force balance, and then mixed with the obtained fired product with grinding in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive
25 firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed
30 by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Further, the fired product was subjected to oxidative firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen
35 and 90% by volume of nitrogen, by raising the temperature at

a rate of 200°C per hour and, after arrival at the maximum temperature of 800°C, maintaining that temperature for 1 hour, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic
5 mortar for 5 minutes. In the above manner, there was obtained an alkaline earth metal aluminate phosphor (A) containing indium in an amount of 0.001 mole as the element In per mole of aluminum.

[0047]

10 (Example 2)

An alkaline earth metal aluminate phosphor (B) containing tungsten in an amount of 0.001 mole as the element W per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.331 g of tungsten(VI) oxide (special
15 reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0048]

(Example 3)

An alkaline earth metal aluminate phosphor (C) containing
20 niobium in an amount of 0.001 mole as the element Nb per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.190 g of niobium(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

25 [0049]

(Example 4)

An alkaline earth metal aluminate phosphor (D) containing bismuth in an amount of 0.001 mole as the element Bi per mole of the aluminum element was obtained in the same manner as in
30 Example 1 except that 0.333 g of bismuth(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0050]

(Example 5)

35 An alkaline earth metal aluminate phosphor (E) containing

molybdenum in an amount of 0.001 mole as the element Mo per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.206 g of molybdenum(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0051]

(Example 6)

An alkaline earth metal aluminate phosphor (F) containing tantalum in an amount of 0.001 mole as the element Ta per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.315 g of tantalum(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0052]

(Example 7)

An alkaline earth metal aluminate phosphor (G) containing thallium in an amount of 0.001 mole as the element Tl per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.326 g of thallium(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0053]

(Example 8)

An alkaline earth metal aluminate phosphor (H) containing bismuth in an amount of 0.001 mole as the element Pb per mole of the aluminum element was obtained in the same manner as in Example 1 except that 0.319 g of lead(II) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0054]

(Example 9)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight),

1.26 g of europium(III) oxide (purity on analysis: 99.6% by weight) and 1.19 g of aluminum fluoride (special reagent grade) were weighed, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The fired product obtained was ground in an automatic mortar for 10 minutes and then subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. Using an electronic force balance, 0.331 g of tungsten(VI) oxide (special reagent grade) was weighed and ground/admixed in an automatic mortar with the fired product obtained as described above for 10 minutes for additive incorporation and simultaneous fired product comminution. The resulting mixture was further subjected to oxidative firing, in an electric oven maintained in an oxidizing atmosphere with a mixed gas composed of 10% by volume of oxygen and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 800°C, maintaining that temperature for 1 hour, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 5 minutes. In this manner, there was obtained an alkaline earth metal aluminate phosphor (I) containing tungsten in an amount of 0.001 mole as the element W per mole of the aluminum element.

[0055]

(Example 10)

An alkaline earth metal aluminate phosphor (J) containing tungsten in an amount of 0.001 mole as the element Mo per mole of the aluminum element was obtained in the same manner as in Example 9 except that 0.206 g of molybdenum(VI) oxide (special reagent grade) was added in lieu of the addition of 0.331 g of tungsten(VI) oxide (special reagent grade).

[0056]

(Example 11)

An alkaline earth metal aluminate phosphor containing niobium in an amount of 0.001 mole as the element Bi per mole of the aluminum element was obtained in the same manner as in Example 9 except that 0.333 g of bismuth(III) oxide (special reagent grade) was added in lieu of the addition of 0.331 g of tungsten(VI) oxide (special reagent grade).

[0057]

(Comparative Example 1)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight), 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium(III) oxide (99.6% by weight), 0.198 g of indium(III) oxide (special reagent grade) and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen

and 90% by volume of nitrogen, by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour.

- 5 The thus-obtained fired product was ground in an automatic mortar for 10 minutes. In the above manner, an alkaline earth metal aluminate phosphor (L) that contained indium in an amount of 0.001 mole as the element In per mole of aluminum element but not fired in any oxidizing atmosphere.

10 [0058]

(Comparative Example 2)

- An alkaline earth metal aluminate phosphor (M) containing tungsten in an amount of 0.001 mole as the element W per mole of the aluminum element was obtained in the same manner as in
15 Comparative Example 1 except that 0.331 g of tungsten(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0059]

(Comparative Example 3)

- 20 An alkaline earth metal aluminate phosphor (N) containing niobium in an amount of 0.001 mole as the element Nb per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.190 g of niobium(V) oxide (special reagent grade) was added in lieu of the addition of
25 0.198 g of indium(III) oxide (special reagent grade).

[0060]

(Comparative Example 4)

- An alkaline earth metal aluminate phosphor (O) containing bismuth in an amount of 0.001 mole as the element Bi per mole
30 of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.333 g of bismuth(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0061]

- 35 (Comparative Example 5)

An alkaline earth metal aluminate phosphor (P) containing molybdenum in an amount of 0.001 mole as the element Mo per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.206 g of molybdenum(VI) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0062]

(Comparative Example 6)

An alkaline earth metal aluminate phosphor (Q) containing tantalum in an amount of 0.001 mole as the element Ta per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.315 g of tantalum(V) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0063]

(Comparative Example 7)

An alkaline earth metal aluminate phosphor (R) containing thallium in an amount of 0.001 mole as the element Tl per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.326 g of thallium(III) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0064]

(Comparative Example 8)

An alkaline earth metal aluminate phosphor (S) containing lead in an amount of 0.001 mole as the element Pb per mole of the aluminum element was obtained in the same manner as in Comparative Example 1 except that 0.319 g of lead(II) oxide (special reagent grade) was added in lieu of the addition of 0.198 g of indium(III) oxide (special reagent grade).

[0065]

(Method of powder whiteness measurement)

Each of the alkaline earth metal aluminate phosphors obtained in Examples 1 to 11 and Comparative Examples 1 to 8 was packed in a vessel with a diameter of 10 mm and a depth of

was packed in a vessel with a diameter of 10 mm and a depth of 5 mm and, after smoothening the surface, the Hunter color model L, a and b values were measured using a color meter (product of Suga Test Instruments; trademark: SM Color Computer, SM-4) and the W value was calculated. The results thus obtained are shown in Table 1.

[0066]

[Table 1]

| | | Element added | Time of addition | Oxidative firing | L | a | b | W |
|--------------|----------------------|---------------|-------------------------------|------------------|------|-------|-------|------|
| 10 15 | Examples | 1 | Just before reductive firing | Done | 94.2 | 0.01 | -2.87 | 93.4 |
| | | 2 | | Done | 94.8 | 0.18 | -2.80 | 94.1 |
| | | 3 | | Done | 93.8 | -0.10 | -3.25 | 93.0 |
| | | 4 | | Done | 91.5 | 0.05 | -2.60 | 91.1 |
| | | 5 | | Done | 91.8 | 0.16 | -2.52 | 91.4 |
| | | 6 | | Done | 94.4 | -0.02 | -2.63 | 93.8 |
| | | 7 | | Done | 90.5 | 0.14 | -3.10 | 90.0 |
| | | 8 | | Done | 94.1 | 0.02 | -2.85 | 93.4 |
| | | 9 | Just before oxidative firing | Done | 94.3 | 0.10 | -3.76 | 93.2 |
| | | 10 | | Done | 94.3 | 0.27 | -4.55 | 92.7 |
| | | 11 | | Done | 95.0 | 0.94 | -3.66 | 93.8 |
| 20 25 | Comparative Examples | 1 | Just before firing in the air | Not done | 88.7 | -0.34 | -4.49 | 87.8 |
| | | 2 | | Not done | 87.6 | 0.15 | -1.40 | 87.5 |
| | | 3 | | Not done | 91.9 | -0.57 | -3.87 | 91.0 |
| | | 4 | | Not done | 70.6 | 0.65 | -1.38 | 70.5 |
| | | 5 | | Not done | 86.7 | 0.11 | -1.60 | 86.7 |
| | | 6 | | Not done | 74.6 | 1.87 | -0.99 | 74.5 |
| | | 7 | | Not done | 85.8 | -0.43 | -5.51 | 84.8 |
| | | 8 | | Not done | 93.0 | 0.55 | -4.06 | 91.9 |

[0067]

Table 1 indicates that the phosphors of the present invention were higher in powder whiteness than the comparative phosphors that contains the respective same additive elements

[0068]

(Comparative Example 9)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight),

73.32 g of aluminum oxide (purity on analysis: 99.27% by weight),
1.26 g of europium(III) oxide (purity on analysis: 99.6% by
weight) and 1.19 g of aluminum fluoride (special reagent grade)
were weighed, and they were mixed up in an automatic mortar
5 (product of Nitto Kagaku Co., ANM-150) for 60 minutes. The
mixture was then placed in an alumina crucible and fired in the
ambient atmosphere by raising the temperature at a rate of 200°C
per hour and, after arrival at the maximum temperature of 1500°C,
maintaining that temperature for 5 hours, followed by
10 temperature lowering at a rate of 200°C per hour. The fired
product obtained was ground in an automatic mortar for 10
minutes and then subjected to reductive firing, in an electric
oven maintained in a reducing atmosphere with a mixed gas
composed of 10% by volume of hydrogen and 90% by volume of
15 nitrogen, by raising the temperature at a rate of 200°C per hour
and, after arrival at the maximum temperature of 1500°C,
maintaining that temperature for 5 hours, followed by
temperature lowering at a rate of 200°C per hour. The resulting
mixture was further subjected to oxidative firing, in an
20 electric oven maintained in an oxidizing atmosphere with a mixed
gas composed of 10% by volume of oxygen and 90% by volume of
nitrogen, by raising the temperature at a rate of 200°C per hour
and, after arrival at the maximum temperature of 800°C,
maintaining that temperature for 1 hour, followed by
25 temperature lowering at a rate of 200°C per hour. Using an
electronic force balance, 0.198 g of indium(III) oxide (special
reagent grade) was weighed and ground/admixed in an automatic
mortar with the fired product obtained as described above for
10 minutes for additive incorporation and simultaneous fired
30 product comminution. In this manner, there was obtained an
alkaline earth metal aluminate phosphor (T) containing indium
in an amount of 0.001 mole as the element In per mole of the
aluminum element.

[0069]

35 (Comparative Example 10)

An alkaline earth metal aluminate phosphor (U) was obtained in the same manner as in Example 1 except that the addition of 0.198 g of indium oxide was omitted.

[0070]

5 (Comparative Example 11)

Using an electronic force balance, 24.11 g of barium carbonate (purity on analysis: 99.39% by weight), 2.1 g of strontium carbonate (purity on analysis: 99.5% by weight), 8.33 g of magnesium hydroxide (purity on analysis: 99.5% by weight),
10 73.32 g of aluminum oxide (purity on analysis: 99.27% by weight), 1.26 g of europium oxide (purity on analysis: 99.6% by weight), and 1.19 g of aluminum fluoride (special reagent grade) were weighed respectively, and they were mixed up in an automatic mortar (product of Nitto Kagaku Co., ANM-150) for 60 minutes.
15 The mixture was then placed in an alumina crucible and fired in the ambient atmosphere by raising the temperature at a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The
20 thus-obtained fired product was ground in an automatic mortar for 10 minutes. Then, the fired product was subjected to reductive firing, in an electric oven maintained in a reducing atmosphere with a mixed gas composed of 10% by volume of hydrogen and 90% by volume of nitrogen, by raising the temperature at
25 a rate of 200°C per hour and, after arrival at the maximum temperature of 1500°C, maintaining that temperature for 5 hours, followed by temperature lowering at a rate of 200°C per hour. The thus-obtained fired product was ground in an automatic mortar for 10 minutes. In the above manner, there was obtained
30 an alkaline earth metal aluminate phosphor (V) not containing any additional element, and not fired in an oxidizing atmosphere.

[0071]

(Method for testing heat resistance and method of deterioration
35 testing by vacuum ultraviolet irradiation)

The phosphors obtained in Examples 1 to 11 and Comparative Examples 9 to 11 were subjected to powder luminance measurement and to deterioration testing by vacuum ultraviolet irradiation. Prior to testing, test specimens were first prepared from the
5 obtained powder-form phosphors themselves in the same manner as in the powder whiteness measurement, and the emissive luminance and emissive chromaticity (y value) of each specimen were measured using an Otsuka Electronics model MCPD-3000 luminance meter. Then, test specimens for ultraviolet
10 irradiation were prepared as follows:

Each of the obtained alkaline earth metal aluminate phosphors was mixed with ethylcellulose (product of Dow Chemical, STD-10) and terpeneol (special reagent grade) in a ratio of 17.5:1:9 on the weight basis, and the mixture was
15 dispersed on a Hoover muller to give a phosphor paste. Each phosphor paste was applied onto a slide glass to give a 2 x 2 cm film with a dry film thickness of 20 μm , and the film was fired in the air at 500°C for 20 minutes to remove the binder and solvent components.

20 The thus-obtained fired films were used as test specimens. At first, luminance and chromaticity (v value) were measured, and then each test specimen was irradiated with ultraviolet rays at 147 nm under vacuum (≤ 5 Pa) for 2 hours using a vacuum ultraviolet lamp (product of Ushio Inc.).

25 [0072]

The difference (emissive chromaticity (y value) of the fired film) - (emissive chromaticity (y value) in powder form) was defined as change in chromaticity (Δy), and the changes were compared. Further, luminance measurements were carried out
30 before and after vacuum ultraviolet irradiation, and the value (luminance after irradiation)/(luminance before irradiation) x 100, which was defined as luminance retention percentage, was calculated for each phosphor, and the extents of deterioration of the respective samples before and after firing were compared
35 based on the luminance retention percentage values obtained.

Submission Date: July 30th, Heisei-15 (2003)

Number=SA61

JP Patent Application No.2003-282828

The results are shown in Table 2. The luminance values shown in Table 2 are relative luminance values converted from the measured luminance values in the respective tests taking the measured luminance value of the powder of Comparative Example

5 9 as 100.

Submission Date: July 30th, Heisei-15 (2003)

Number=SA61

JP Patent Application No.2003-282828

[0073]

[Table 2]

| | | Element added | Time of addition | Oxidative firing | Powder luminance | Film luminance | After vacuum UV irradiation | Luminance retention | Change in chromaticity |
|---------------------|----|---------------|------------------------------|------------------|------------------|----------------|-----------------------------|---------------------|------------------------|
| Example | 1 | In | Just before reductive firing | Done | 106 | 104 | 97 | 93 | 0.004 |
| | 2 | W | | Done | 110 | 108 | 105 | 97 | 0.000 |
| | 3 | Nb | | Done | 112 | 111 | 108 | 97 | 0.001 |
| | 4 | Bi | | Done | 101 | 99 | 94 | 95 | 0.002 |
| | 5 | Mo | | Done | 105 | 103 | 97 | 94 | 0.002 |
| | 6 | Ta | | Done | 100 | 99 | 90 | 91 | 0.003 |
| | 7 | Tl | | Done | 106 | 102 | 94 | 92 | 0.003 |
| | 8 | Pb | | Done | 103 | 98 | 90 | 92 | 0.004 |
| | 9 | W | Just before oxidative firing | Done | 115 | 113 | 108 | 96 | 0.000 |
| | 10 | Mo | | Done | 102 | 101 | 96 | 95 | 0.001 |
| | 11 | Bi | | Done | 98 | 97 | 90 | 93 | 0.001 |
| Comparative Example | 9 | In | After firing | Done | 99 | 96 | 84 | 88 | 0.006 |
| | 10 | - | - | Done | 100 | 97 | 86 | 89 | 0.006 |
| | 11 | - | - | Not done | 130 | 116 | 98 | 83 | 0.031 |

[0074]

It was shown that the phosphors obtained in the Examples showed improvements, by at least 10%, in luminance after vacuum ultraviolet irradiation, hence markedly reduced
5 deteriorations due to vacuum ultraviolet rays, as compared with the phosphors obtained in the Comparative Examples. It was also shown that the luminance was high but the luminous color shifting was remarkable in Comparative Example 11, whereas the phosphors of Examples 1 to 11 showed very slight changes in
10 emitted light chromaticity, indicating the prevention of luminous color shifting.

It was further shown that the phosphors of Examples 1 to 8 and the phosphors of Examples 9 to 11 showed improved luminance values after vacuum ultraviolet irradiation and very great
15 extents of deterioration prevention in spite of the different steps of addition of indium, tungsten, niobium, bismuth, molybdenum, tantalum, thallium and lead, respectively. However, Comparative Example 9, in which indium was added after firing in an oxidizing atmosphere of the last step did not show
20 inhibiting effect of deterioration. In addition, Comparative Example 9 showed decrease of luminance.

[INDUSTRIAL APPLICABILITY]

[0075]

The alkaline earth metal aluminate phosphor of the
25 invention is a phosphor excellent in luminance retention performance with the deterioration with time and the luminous color shifting upon heating and vacuum ultraviolet irradiation being markedly suppressed and, therefore, when it is applied in manufacturing PDPs and the like, the deterioration thereof
30 in the manufacturing process can be prevented. Furthermore, the alkaline earth metal aluminate phosphor of the invention is a phosphor showing a high powder whiteness and excellent in fluorescence reflecting properties and therefore causes no
35 function lowering due to the absorption of the fluorescence emitted.

[Document Name] Abstract

[Abstract]

[Subject] To provide an alkaline earth metal aluminate phosphor that does not cause luminance decreases and emission shifting but have good heat resistance durability against vacuum ultraviolet rays and ultraviolet rays, and high powder whiteness. It is another object of the present invention to provide a method of producing the same.

[Means for solving] An alkaline earth metal aluminate phosphor containing bivalent europium as an activator, which is obtained by a process comprising: a step (1) of mixing a fired product (A) with a compound (B), the fired product (A) comprising barium and/or strontium(a), magnesium(b), aluminum(c) and europium(d), the compound (B) being at least one compound selected from the group consisting of indium compounds, tungsten compounds, niobium compounds, bismuth compounds, molybdenum compounds, tantalum compound, thallium compounds and lead compounds; and a step (2) of firing, in an oxidizing atmosphere, the mixture obtained in the step (1) or a fired product of the mixture obtained in the step (1), the step (2) being preceded, at least once, by firing in a reducing atmosphere.

[Selective Figure] None

Submission Date: April 3rd, Heisei-15 (2003)
Number=SA58 JP Patent Application No.2003-100646

[Document Name] Patent Application
[Filing Number] SA58
[To] Commissioner, Patent Office
[IPC] C09K 11/08
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] HIRAYAMA Seiko
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] KOBAYASHI Keita
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] ISHII Junya
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] WADA Mizuho
[Inventor]
[Address or Residence] c/o Sakai Chemical Industry Co., Ltd.,
5-1, Ebisujimacho, Sakai-shi, Osaka
[Name] NAKAHARA Shinji
[Applicant]
[Identification Number] 000174541
[Name] Sakai Chemical Industry Co., Ltd.
[Agent]
[Identification Number] 100086586
[Patent Attorney]
[Name] YASUTOMI Yasuo
[Appointed Agent]
[Identification Number] 1000120019
[Patent Attorney]
[Name] YAGI Toshiyasu

Submission Date: April 3rd, Heisei-15 (2003)
Number=SA58 JP Patent Application No.2003-100646

[Indication of Fee]

[Number of Deposit Ledger] 033891

[Amount of Payment] 21,000 yen

[List of Attached Documents]

[Document Name] Specification 1

[Document Name] Abstract 1

[The Number of General Power of Attorney] 0004000